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NASA TECHNICAL MEMORANDUM

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METHOD FOR PRODUCING HEAT-RESISTANT SEMI-
INORGANIC COMPOUNDS

S. Yajima, K. Okamura,
T. Shishido and Y. Hasegawa



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Hitzebeständigen Halbanorganischen Verbindungen."
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16. Abstract Discusses the method for producing a heat- resistant, semi-inorganic compound. Provides five examples in which various alcohols, phenols, and aromatic carbonic acids are used to test heat re- sistance and solubility.			
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Applicant: The Research Institute for Special Inorganic
Materials, Ibaragi (Japan)

Representative: Tiedtke, H., Dipl.-Eng.; Buhling, G., Dipl. -Chem;
Kinne, R., Dipl.-Eng.; Grupe, P., Dipl.-Eng;
Pellmann, H. B., Dipl.-Eng.; patent attorneys,
8000 Munchen

Inventors: Yajima, Seishi; Okamura, Kiyohito; Shishido, Toetsu;
Hasegawa, Yoshio; Ibaragi (Japan)

Patent Claims

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1. Method for producing a heat-resistant semi-inorganic compound, characterized by reacting an organoborosiloxane compound at a temperature of 250-450°C in an atmosphere inert with respect to the reaction, with at least one organic compound chosen from aliphatic polyvalent alcohols, aromatic alcohols, phenols and aromatic carbonic acids.
2. Method following Claim 1, characterized by employing the organic compound in a quantity of 0.1 to 3 mole per mole of the organoborosiloxane.
3. Method following Claim 1 or 2, characterized by carrying out the reaction in the absence of a solvent or diluting agent.

* Numbers in margin indicate pagination of foreign text.

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/2

Asahi-Mura, Kashima-Gun / Japan

Method for Producing Heat-Resistant Semi-
Inorganic Compounds

The invention refers to a method for producing heat-resistant semi-inorganic compounds.

Examples of known methods for producing organoborosiloxane compounds, one class of semi-inorganic compound, are the dehydrocondensation reaction of boric acid with a silandial, the condensation reaction of boric acid with a diorganodichlorsilane proceeding under the splitting off of hydrogen chloride, the condensation reaction of boric acid with a diorganodialkoxysilane proceeding under dealcoholization, and the condensation reaction of a boric acid ester with a diorganodialkoxysilane proceeding under de-esterization. From U. S. Patent application 2,517,945, a method for producing an organoborosiloxane compound is known in which a difunctional boric acid such as phenylboric acid, which is employed in place of the trifunctional boric acid, is reacted with diphenylsilandiol at a temperature of 170-260°C.

/3

The inventors had found earlier that an organoborosiloxane polymer with at least one phenyl group bound to a silicon atom has a much better heat resistance than the organoborosiloxane compounds which were known up to that time. The phenyl-containing organoborosiloxane polymer and a method for its production are disclosed in U. S. Patent application no. 835,373, filed on September 21, 1977. It is assumed that the heat resistance of the phenyl-containing organoborosiloxane polymer is attributable to its three-dimensional network structure. This organoborosiloxane polymer, however, has the drawback in that its softening temperature extraordinarily sharply

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increases and, that it can be dissolved with difficulty in a solvent when the polymer is given a high degree of network structure in order to increase its heat resistance. For that reason, its workability is reduced when it is employed as raw material for a heat-resistant material. The phenyl-group-containing organoborosiloxane polymer suggested earlier by the inventors is therefore not completely satisfactory.

In connection with the invention, extensive investigations were undertaken in which it was found that a semi-inorganic compound with superior heat resistance can be obtained which is easily soluble and which exhibits a borosiloxane bond by reacting an organoborosiloxane compound with at least one specified organic compound chosen from aliphatic polyvalent alcohols, aromatic alcohols, phenols and aromatic carbonic acids. Because the semi-inorganic compound obtained by the invented method is easily soluble in a solvent, it 4 has very good workability and is suited for raw material for various heat-resistant materials.

The subject of the invention is a method for producing a heat-resistant semi-inorganic compound, characterized by reacting an organoborosiloxane compound at a temperature of 250-450°C, in an atmosphere inert with respect to the reaction, with at least one organic compound chosen from aliphatic polyvalent alcohols, aromatic alcohols, phenols and aromatic carbonic acids.

The accompanying illustrations are briefly explained below.

Figure 1 shows an infrared absorption spectrum of the heat-resistant semi-inorganic compound synthesized in example 3 below.

Figure 2 shows in Curve I a thermogravimetric curve of the heat-resistant semi-inorganic compound synthesized in example 4 below and for comparison, in Curve II

a thermogravimetric curve of a known polyborodiphenylsiloxane.

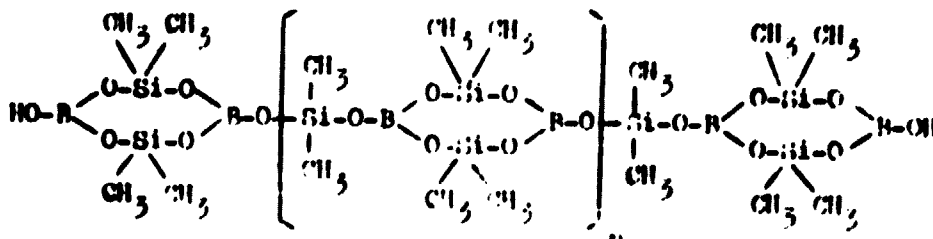
The invention is explained more closely below.

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The organoborosiloxane compound employed as a starting material in the invented method is a semi-inorganic compound (i.e., an organic-inorganic compound), in which a boron atom is bound to a silicon atom via an oxygen atom and in which the organic group is bound to the silicon atom as a side group. Such organoborosiloxane compounds are known in themselves.

The organoborosiloxane compound can be produced, for example, by the dehydrocondensation reaction of boric acid with a silandial, the condensation reaction of boric acid with a diorganodichlorsilane proceeding under the splitting off of hydrogen chloride, the condensation reaction of boric acid with a diorganodialkoxysilane proceeding under dealcoholization, and the condensation reaction of a boric acid ester with a diorganodialkoxysilane proceeding under de-esterization. In addition, in order to produce an organoborosiloxane compound, a trifunctional silane such as trichlorophenylsilane can be reacted with boric acid, instead of using the reaction of the above mentioned difunctional silanes with boric acid.

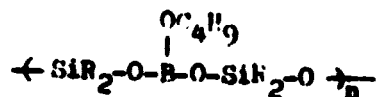
R. L. Vale reports in J. Chem. Soc., 2252 (1960) on the production of a borosiloxane compound of the formula given below, by the condensation reaction of dichlordimethylsilane with boric acid, proceeding under the splitting off of hydrogen chloride.



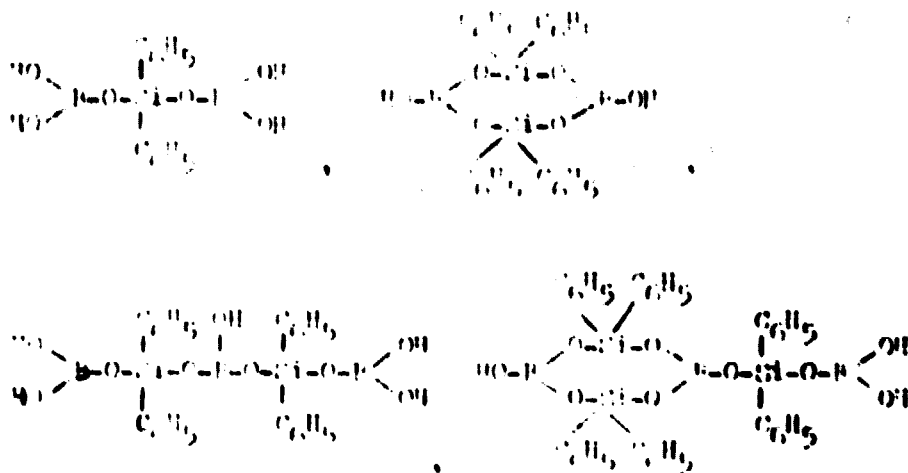
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As reported, this compound has a molecular weight of 500 to 1000, which was obtained from elemental analysis, determination of the quantity of hydrogen chloride created, ebullioscopy, and cryoscopy.

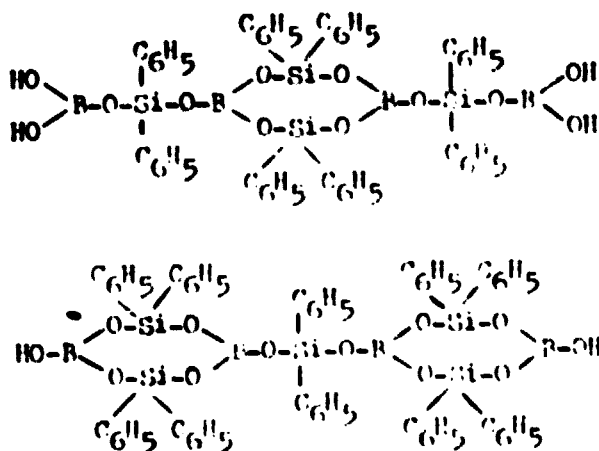
K. A. Andrianov and L. M. Volkova report in Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, 303 (1957), on the production of a borosiloxane compound by the polycondensation of an alkyl or aryl dialkoxysilane with triacetoxyboron or the polycondensation of an alkyl or aryl diacetoxysilane with butyl borate. The reaction product of the latter polycondensation is represented for example by the following formula:



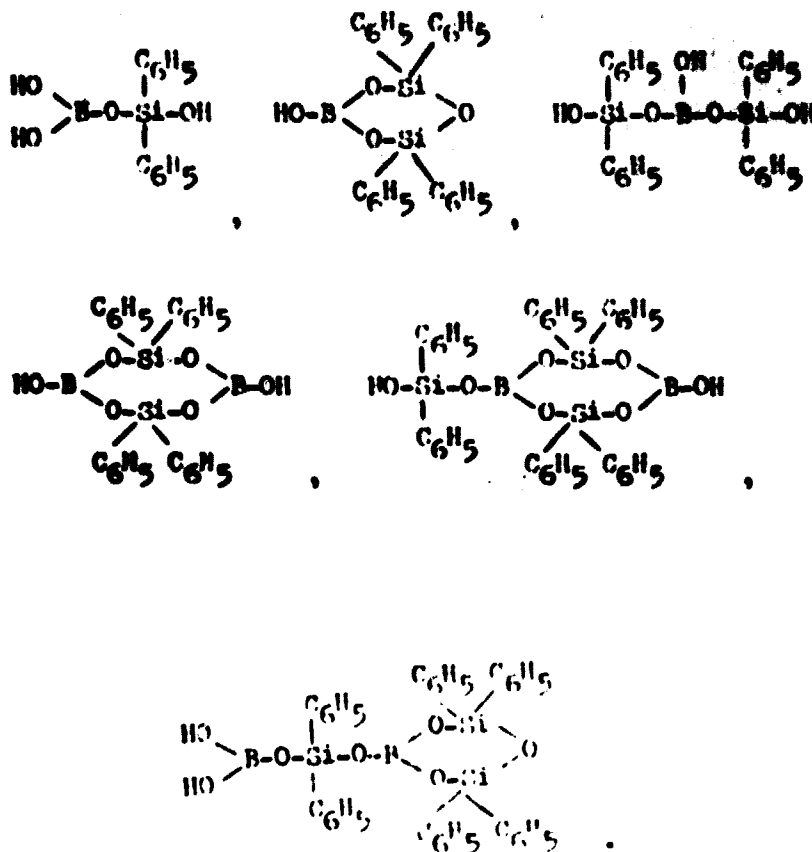
In the U. S. Patent application no. 835,373, which was submitted earlier by the inventors, a process for synthesizing polyborodiphenylsiloxane by the polycondensation of diphenyldichlorsilane or diphenylsilandiol with boric acid is published. When the reaction in this polycondensation process is carried out in benzol or n-butyl ether, one obtains a borodiphenylsiloxane compound with low molecular weight as an intermediate product. When the intermediate product is, for example, heated to 400°C, a polyborodiphenylsiloxane results, with a molecular weight of 500 to 10,000 and a high degree of cross-connection. The molecular weight of the intermediate product can be measured by gel permeation chromatography (GPC), ebullioscopy, cryoscopy, etc., and it was found that it is less than about 1000. Infrared absorption spectroscopy or elemental analysis show that the reaction product formed by reacting diphenyldichlorsilane and boric acid contains compounds with the following structures: /7



8



It is assumed that the reaction product formed by reacting diphenylsilandiol and boric acid contains compounds with the following structures:



29

Through the addition of a small amount of a monofunctional silane such as triphenylchlorosilane or triphenylsilanol to the reaction described above, the molecular weight of the resulting organoborosiloxane compound can be lowered.

The organoborosiloxane employed as a starting material in the invented process is produced by the condensation reaction of a silane derivative component which consists mainly of a silane derivative and which contains, if necessary, a small amount of a mono or trifunctional silane derivative, with a boric acid component which consists of boric acid or a boric acid derivative. The reaction product is in general, not a single compound, but is obtained in the form of a mixture of many compounds with a borosiloxane bond. The organoborosiloxane compound employed in the invention can be a single compound or a mixture of many organoborosiloxane compounds. It is difficult to determine the structures of the individual compounds in

the mixture and their proportions in the mixture. The average molecular weight of the mixture can be established by a common procedure for measuring molecular weights, for example, by ebullioscopy or cryoscopy.

/10

The organic side-chain group bound to the silicon atom of the organoborosiloxane compound employed in the invented process can be a hydrocarbon group, for example, an alkyl group such as methyl or ethyl, a cyclic alkyl group such as cyclohexyl or an aryl group such as phenyl. The phenyl group is especially preferred. An organoborosiloxane compound with a highly developed network structure is undesirable for use in the invented process because its reactivity with the aliphatic polyvalent alcohol, the aromatic alcohol, the phenol or the aromatic carbonic acid is reduced. The organoborosiloxane compound employed as starting material generally has, in preference, molecules with a size which corresponds to a monomer or at most, an oligomer. Such an organoborosiloxane compound with a relatively small average molecular weight can be produced by lowering the reaction temperature or employing a monofunctional organosilane derivative. The organoborosiloxane compound employed in the invention has an average molecular weight of generally not more than about 2000, preferably not more than 1300.

The organic compound to be reacted with the organoborosiloxane in the invented process is at least one compound selected from aliphatic polyvalent alcohols, aromatic alcohols, phenols and aromatic carbonic acids. The desired heat-resistant semi-inorganic compound which contains a borosiloxane bond can be obtained by mixing the organic compound thoroughly with the organoborosiloxane compound, and reacting the mixture at a temperature of 250-450°C in an atmosphere which is inert with respect to the reaction.

/11

Suitable aliphatic polyvalent alcohols for use in the invented process are ethylene glycol and glycerine. A suitable aromatic alcohol is benzyl alcohol. In general, the resulting compound tends

toward a lower softening temperature and to poorer heat resistance with an increasing number of carbon atoms in the hydrocarbon chain.

Examples of the phenols are phenol, pyrocatechol, resorcin, hydroquinone, orcin, pyrogallol, phloroglucin, hydroxyhydroquinone, cresol, thymol, carvacrol, bisphenol A, naphthol, binaphthol, anthrol and anthrahydroquinone.

Examples of the aromatic carbonic acids are benzoic acid, phthalic acid, isophthalic acid and terephthalic acid.

Among these organic compounds the aromatic alcohols, the phenols and the aromatic carbonic acids and especially the phenols, are generally preferred. Among the phenols, phenol and hydroquinone are preferred.

The quantity of the organic compound amounts generally to 0.1 to 3 mole, preferably 0.1 to 1 mole, per mole of the organoboro-siloxane compound. When the quantity lies under 0.1 mole, the resulting compound shows no appreciable increase in heat resistance; when it lies above 3 moles, unreacted compounds remain, or else the heat resistance of the resulting product is reduced.

/12

The reason for restricting the reaction temperature in the invented process to 250-450°C lies in the fact that the reaction does not proceed sufficiently under 250°C, while over 450°C, it leads to a breakup of the borosiloxane bond or to conversion into an inorganic material. By conversion to an inorganic material is meant the phenomenon that thermal breakup, liberation of the organic side-chain groups, or the development of a three-dimensional network structure through cross-connection sets in, and that thereby the hydrogen content appreciably decreases so that the reaction product is transformed into an inorganic ceramic material which consists mainly of silicon, oxygen, boron and carbon.

The reaction can be carried out in the invented process in the presence of a solvent or diluting agent. In general, it is preferred to mix the organopolyborosiloxane and the organic compound thoroughly without using a solvent or diluting agent and to react the resulting mixture at the given temperature in an inert atmosphere.

The heating of the mixture of reaction participants is begun preferably at room temperature and the mixture is brought to the given temperature at a suitable rate of temperature increase. The suitable rate of temperature increase depends on the type of organic compound and its exact determination is difficult. A suitable rate of temperature increase is one in which no vaporization of the aliphatic or aromatic alcohol, or no sublimation of the phenol or the aromatic carbonic acid sets in so that the evaporation without /13 reaction of the organic compound from the reaction system is avoided.

In the invented process, it is essential that the reaction of the organic compound with the organoborosiloxane compound is carried out in an atmosphere which is inert with respect to the reaction. The inert atmosphere consists preferably of an inert gas such as nitrogen or a noble gas such as argon. The use of reduced pressure is undesirable since the compounds produced will be removed from the reaction system. The reaction is generally carried out under atmospheric pressure. The use of an oxidizing atmosphere such as air is undesirable, since oxidation will set in during the reaction.

The softening temperature of the heat-resistant semi-inorganic compound can be regulated by suitably choosing the reaction temperature and/or the reaction time in carrying out the invented process. In general, the softening temperature increases with higher reaction temperature and longer reaction time.

It is not yet completely clear which reactions take place in the invented reaction of the organoborosiloxane compound with the organic compound (i.e., the aliphatic polyvalent alcohol, the phenol

or the aromatic carbonic acid). Very complicated reactions are probably involved. Possibly a reaction of the organic compound with the OH-group bound to a boron or silicon atom, a ring-opening reaction (if the organoborosiloxane compound is a cyclic compound), a splitting of the Si-O-B bond, and other reactions take place, and it is assumed that these reactions concur with each other in giving rise to a very complicated total reaction.

/14

The heat-resistant semi-inorganic compound obtained in the invented process is described more closely below.

While known heat-resistant polymers such as completely aromatic polyamides and teflon (tetrafluorethylene-fluorohydrocarbons) find only limited usage because of their insolubility in solvents or as a result of the fact that they decompose without softening for which reason they have poor workability, the heat-resistant semi-inorganic compound obtained in the invented process dissolves easily in organic solvents such as tetrahydrofuran; it softens at high temperatures and can be shaped easily by forming various objects. The thermogravimetric analysis shows that the invented semi-inorganic compound hardly reacts with oxygen up to a temperature of about 450°C and has a high resistance of oxidation. It can therefore be employed as a binder for various ceramic or metal powders or as a coloring agent, and can be anticipated as a new heat-resistant material. If desired, the invented compound can have an increased softening temperature, and it can in addition be hardened through the effect of heat, by heating it to a temperature which lies above its original softening temperature. In this manner, materials with higher heat resistance can be produced by working the invented semi-inorganic material at a relatively low temperature and subjecting it to a heat treatment.

/15

The invention will be explained more closely through the following examples.

Example 1

A 5-liter flask was charged with 310 g boric acid, 1898 g diphenyldichlorsilane and 3 liters n-butyl ether, and the mixture was reacted for 18 hours under agitation at 100°C. The reaction mixture was cooled down, whereupon a white precipitate formed. The n-butyl ether was removed and the precipitate was washed with methanol in order to remove the unreacted boric acid. The remains were further washed with water and 1680 g of a borodiphenylsiloxane compound were obtained, with an average molecular weight (median) of about 400 which was employed as a starting material in the invented process.

27 g of ethylene glycol were thoroughly mixed with 200 g of the obtained borodiphenylsiloxane. The mixture was heated at a rate of 120°C/hour in a 500 ml flask under agitation in a nitrogen atmosphere. The mixture was reacted for one hour at 350°C whereupon a brown resin-like compound was obtained.

This compound dissolved easily in tetrahydrofurane and softened at 150°C. When the mixture was heated at a rate of 5°C/min for the thermogravimetric analysis in a nitrogen atmosphere, it was found that weight loss began at 225°C, that the weight loss reached 5% at 320°C, and that the proportion of weight remaining at 800°C amounted to 54%. /16

Example 2

22 g of benzyl alcohol were mixed thoroughly with 200 g of the borodiphenylsiloxane compound produced in Example 1. The mixture was heated at a rate of 100°C/hour in a 500 ml flask with agitation in a nitrogen atmosphere and heated for one hour at 400°C, whereupon a brown, resin-like compound was obtained.

The compound dissolved easily in tetrahydrofurane and softened at 180°C. In thermogravimetric analysis of the compound, it was

found that weight loss began at 260°C and reached 5% at 350°C. The proportion of weight remaining at 800°C amounted to 60%.

Example 3

20 g of phenol were mixed thoroughly with 200 g of the borodiphenylsiloxane compound synthesized in Example 1. The mixture was heated at a rate of 55°C/hour in a 500 ml flask in a nitrogen atmosphere with agitation and reacted for one hour at 450°C, whereupon a light yellow, resin-like compound was obtained.

The compound dissolved easily in tetrahydrofurane and softened at 230°C. In thermogravimetric analysis, it was found that weight loss began at 340°C and reached 5% at 460°C, and that the proportion of weight remaining at 800°C amounted to 64.6%. The infrared absorption spectrum of this compound is shown in Figure 1. This /17 spectrum shows the absorptions given below which are characteristic of the heat-resistant, semi-inorganic compounds which are obtained in the invented process:

3220 cm^{-1} (this absorption is ascribable to the O-H bond of B-OH or SiOH); 1350 cm^{-1} (this absorption is ascribable to the O-B bond of Si-O-B); 1080 cm^{-1} (this absorption is ascribable to the Si-O bond of Si-O-B or Si-O-Si).

Example 4

20 g of hydroquinone were mixed thoroughly with the borodiphenylsiloxane compound produced in Example 1. The mixture was heated at a rate of 50°C/hour in a 500 ml flask in a nitrogen atmosphere with agitation and reacted for one hour at 300°C whereupon a light yellow, resin-like compound was obtained.

This compound dissolved easily in tetrahydrofurane and softened at 180°C. Thermogravimetric analysis revealed that weight loss set in at 300°C and reached 5% at 440°C, and that the proportion of

weight remaining at 800°C amounted to 65.5%.

The two thermogravimetric curves in Figure 2 (measured in a nitrogen atmosphere at a temperature increase rate of 5°C/hour) illustrate the fact that the heat resistance of the borodiphenylsiloxane is appreciably increased by its reaction with hydroquinone. Curve I refers to the heat-resistant semi-inorganic compound obtained in Example 4. Curve II refers to a heat-resistant polyborodiphenylsiloxane which softens at 130°C and was obtained by /18 heating the borodiphenylsiloxane compound produced in Example 1 at a rate of 50°C/hour in a 500-ml flask in a nitrogen atmosphere with agitation and then by heating it for one hour at 400°C, in order to effect a polycondensation of the compound. It follows clearly from the experimental results shown in Figure 2 that the borodiphenylsiloxane compound can be given a much higher heat resistance by heating it to 300°C in the presence of hydroquinone, instead of heating it to 400°C in the absence of hydroquinone.

Example 5

20 g of terephthalic acid were mixed with 200 g of the borodiphenylsiloxane compound synthesized in Example 1. The mixture was heated at a rate of 100°C/hour in a 500-ml flask in a nitrogen atmosphere with agitation and the heating was stopped when the temperature reached 350°C. In this manner a light yellow, resin-like compound was formed.

This compound dissolved easily in tetrahydrofurane and softened at 260°C. Thermogravimetric analysis revealed that weight loss set in at 280°C and reached 5% at 360°C, and that the proportion of weight remaining at 800°C amounted to 67%.

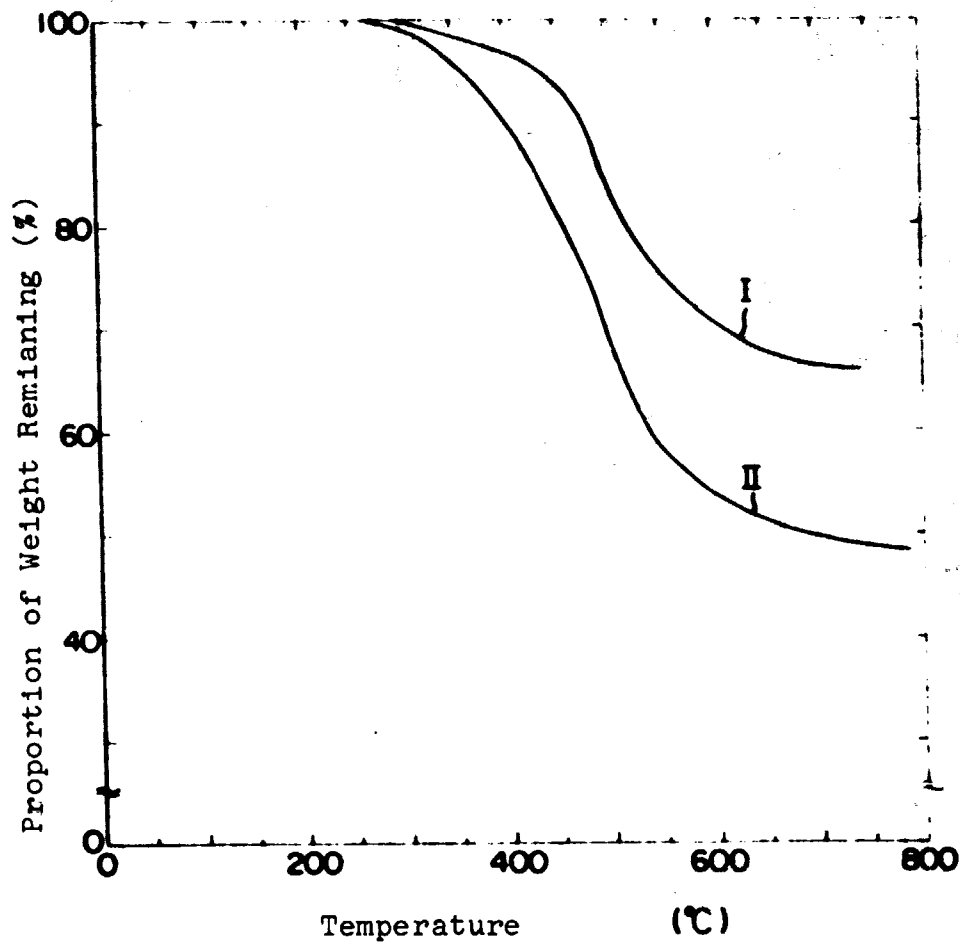


Fig. 1

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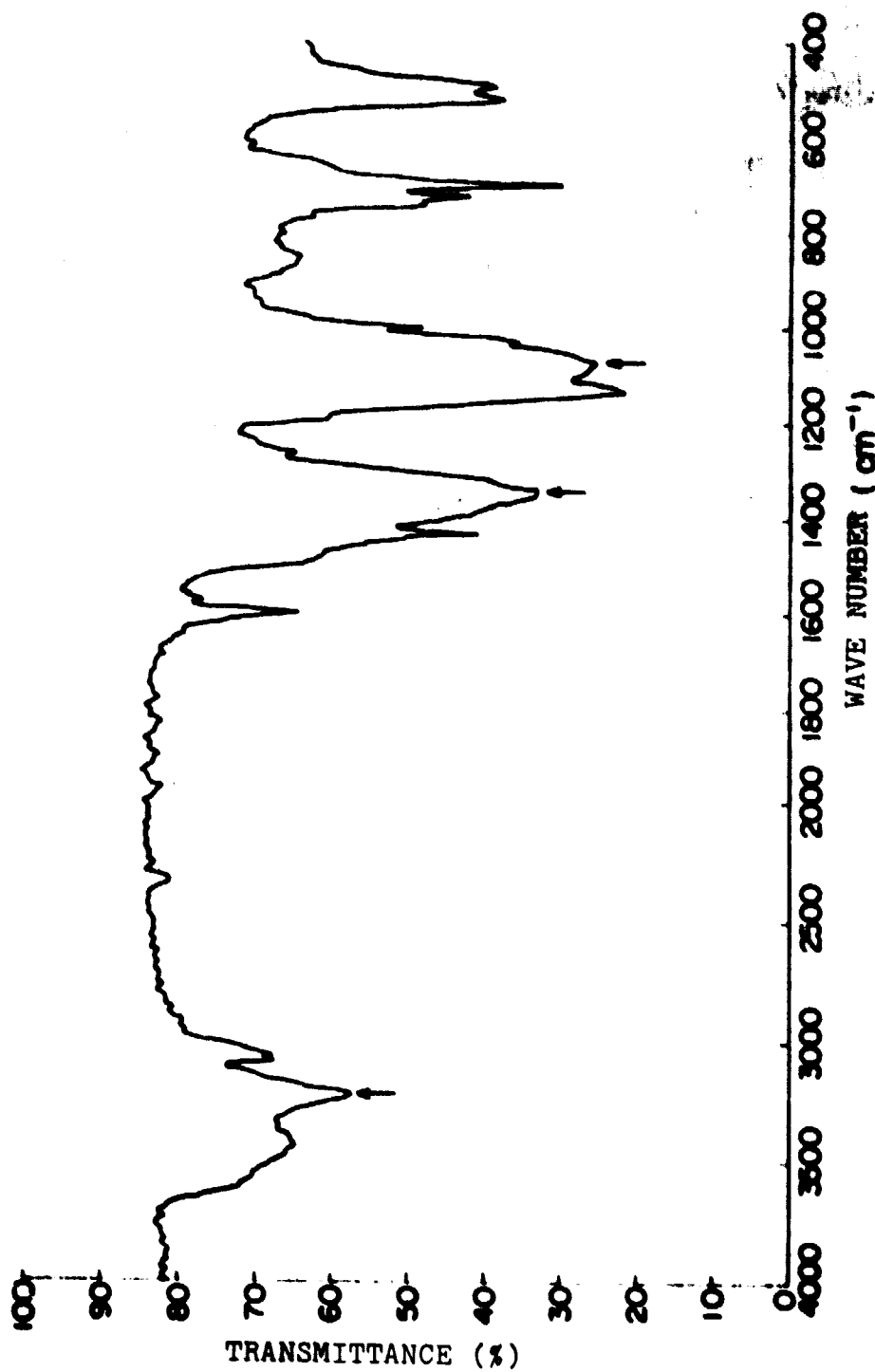


Fig. 2